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THE SOLUBILITY OF LIQUIDS IN LIQUIDS. THE PARTITION OF THE LOWER ACIDS BETWEEN WATER AND COTTONSEED OIL. ALSO THE PARTITION OF FORMIC ACID BETWEEN WATER AND VARIOUS ORGANIC COMPOUNDS.

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CONTENTS

page

Acknowledgment---------- 3

Introduction---------- 4

Material---------- 7

Procedure---------- 10

Results---------- ---------- 11

Tables----------13-31

Discussion of Results---------- 32

Graphs---------- 35

Summary---------- 41

Biography---------- 43

Acknowledgment.

This investigation, having been carried out under the advice and kind assistance of Doctor Reid, I take this opportunity to express my deep appreciation for the help he has given me. I also feel under obligation to Drs. Frazer, Remsen, Lovelace and Gilpin, for instruction and encouragement received. I shall long remember the enthusiastic personality of the late Doctor Jones, who inspired me to take up graduate work at the Johns Hopkins University.

I am greatly indebted to Mr. Smith, Headmaster of the Park School, who so kindly arranged my teaching that my graduate work was made possible.

THE SOLUBILITY OF LIQUIDS IN LIQUIDS. THE PARTITION OF THE LOWER ACIDS BETWEEN WATER AND COTTONSEED OIL. ALSO THE PARTITION OF FORMIC ACID BETWEEN WATER AND VARIOUS ORGANIC COMPOUNDS.

Introduction.

Work, was recently begun in this laboratory by Wroth and Reid[1] with a purpose of gaining an idea of what is meant by infinite solubility. The lower alcohols were partitioned between cottonseed oil and water; and the partition law,

$$\frac{Ca}{Cb} = r = \frac{Sa}{Sb}$$

as worked out by Jakowkin[2] was used where Ca and Cb are the concentration of C, the solute in the solvents A and B, respectively, r is a constant ratio, and Sa and Sb are the solubilities of the solute in the two solvents.

Jakowkin determined the partition coefficient in the case of iodine and bromine, between water and (1) carbon disulphide, (2) bromoform, (3) carbon tetrachloride. With carbon disulphide and water, a marked decrease of

1. J. Am. Chem. Soc. 38, 2316 (1916).

2. Zeit. physikal. chem., 18, 590 (1895).

the partition ratio occurs with dilution, probably owing to the decomposition of complex molecules. A similar decrease occurs with bromoform, but with carbon tetrachloride, the ratio remains almost constant. In saturated solution, the partition coefficient should be equal to the ratio of the solubilities in the two solvents, and the following table shows that this is the case.

Water and ;	Solubility ratio;	Partition coefficient.
Carbon disulphide:	679.0 :	685.0
Bromoform .....:	559.0 :	558.5
Carbon tetrachloride:	89.6 :	89.7

In this work it is necessary to have the solvents A and B immiscible . Steiner[1] and Gordon[2] have shown that the solubility of gases in water are much altered by the presence of even small amounts of salts in solution. More recent work is by Marden and Dover[3] where the solubility of lithium chloride in ethyl acetate is decreased about 90% by the presence of 10% of benzene. This plainly shows that if any appreciable amount of A

1. Wied. Ann. 52, 275 (1894).
2. Z. physik chem. 18, 520 (1895).
3. Am. chem. Soc., 39, 1 (1917).

dissolves in B, the solvent power of B for C is thereby altered and "vice versa". In this case Sa and Sb would be the solubilities of C in A saturated solubilities in the pure solvent.

Waddell [1] in studying the partition of acetic acid between benzene and water, noted that, when much acetic acid is present, the water dissolves considerable benzene and vice versa. The solubility of acetic acid in benzene containing considerable water would doubtless be quite different from its solubility in dry benzene.

The formula $Ca/Cb = r = Sa/Sb$ as given above has five quantities, but since it is a double equation, it is only necessary to determine three of them in order to calculate the other two. Simply, measure Ca and Cb and consequently find r, and then measure Sa, and Sb is calculated at once.

This suggests a method for finding solubility numbers for very soluble liquids, provided that we have ideal conditions, i.e. that the solvents A and B are totally insoluble in each other even when considerable amounts of the solute are present, and the presence of the one does not influence the solubility of the solute in the other and that there is no polymerization, dis-

1. Jour. phys. chem., 2, 233, 1898.

sociation or other change of the solute in either of the solvents.

Of course these conditions are, at best, only approximated in any actual case and hence the equation above can give only approximate results. Ostwald's dilution law has rendered valuable service in the study of conductivities, though it holds strictly for ideal solutions only and the solutions with which we actually work only approximate ideal ones. The closer we get to ideal solutions the closer does the dilution law hold, and the same may be expected of solubility relations.

In the previous study the lower alcohols were partitioned between, water and cottonseed oil. In the first part of the present investigation the lower fatty acids were partitioned between water and cottonseed oil while, in the second part, formic acid was partitioned between water and benzene, toluene, carbontetrachloride, carbonbisulphide, and bromoform to find to what extent the figures for the solubility of formic acid in water, obtained by the use of various solvents, agree.

MATERIAL.

Cottonseed Oil : The Wessen oil was used. It was found to have an acid reaction. In order to eliminate this acid, it was shaken with a dilute solution of barium

hydroxide for an hour. It was then centrifuged and filtered, when it gave a perfectly neutral reaction.

Formic Acid: It was distilled under reduced pressure over anhydrous copper sulphate. The pressure used was 120 mm, when the acid distilled over at 50° . This method was found to be a very satisfactory one. Beginning with an acid 89.2 percent pure, the first distillation results in an acid 96.5 percent, the second 98.2 percent, and the third distillation gave an acid 99.99 percent pure. This acid melted at 8.35°. The specific gravity was found to be $1.2170^{\frac{15}{25}}$. [1*] This anhydrous acid was only used for the solubility work. For the partition work commercial acid was used since it was found to contain only water. The water it contained was calculated and added to the water layer.

Acetic Acid : Like formic acid the commercial acid was used for the partition work. For the solubility the acid was purified by freezing. It was found that the number of times it took to freeze it anhydrous could be cut down by introducing a crystal of the acid and thus prevent too great undercooling. It melted at 16.7 , and titrated 99.9 percent pure. Its density was 1.0445

Propionic and Butyric Acids: These acids were infinitely soluble in both oil and water and thus it was

1. Amer. Chem. Jour. 46, (1911); J. 1086, 216.

*. J. Chem. Soc. 588 (1908).

not necessary to make them anhydrons. As their densities showed they contained only water as an impurity, they were used without purification.

Isovaleric Acid: This acid was distilled four times over anhydrous copper sulphate, when it was found to titrate 99.98 percent pure, and had a density of $0.937^{\frac{25}{25}}$.

Organic Solvents: First class commerical grades of Benzene, toluene, Xylene, Carbontetrachloride, Carbondisulphide, and Bromeform were used. To insure purity, the boiling points and densities were taken and found to agree well with those given in the literature.

Waddell found in his investigation that the same partition coefficient was given with purified benzene as with commercial benzene.

Standard Solutions: Standard solutions of approximately m/10 were prepared, and frequently standardized . The solutions were kept in large stock bottles from which the solutions were siphoned into their respective burettes. The top of the Barium Hydroxide bottle and burette were protected from the air by tubes containing soda lime.

Water : Freshly distilled water was used.

Kerosene Oil: Commercial kerosene oil was distilled and the portion obtained between 180° C and 260° C was used in the partition work. It had a density of $0.798^{\frac{25}{25}}$.

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1. Jour. phys. chem. 2, 233, 1895.

PROCEDURE

The filling, shaking and centrifuging of the bottles containing cottonseed oil, water and the respective acids was carried out approximately as the former work where the alcohols were used instead of the acids. It seemed necessary to shake the acids longer than the alcohols to obtain concordant results. The centrifuge was only used with the cottonseed oil and water.

Estimation of Acids in Oil and Hydrocarbon Layers: The oil layer containing the acid was drawn off by means of a special pipet, shaped on the order of the Ostwald pycnometer. An amount of oil was taken out with the pipet sufficient to require about 10 cc. of the barium hydroxide for neutralization. The oil was put in a 150 cc. beaker containing about 80 cc. of distilled water for titration. The oil, with ordinary stirring, failed to give up its acid promptly making the titration slow and uncertain.

A mechanical stirrer was used and this accelerated the speed with which the acid passed from the oil into the water. Even under these conditions the end point was not accurate as it was in the water. In spite of all efforts the oil seemed to have a slight tendency to cling to the acid. The organic solvents were handled

similarly to the oil layer.

Estimation of Acid in Water Layer: A small thin-walled glass bulb was weighed, partly filled from the water layer, sealed and reweighed. The bulb was then broken under water to avoid evaporation, and the amount of acid, which it contained was determined by titration.

The absolute solubilities of formic acid and acetic acid in cottonseed oil were found by shaking the cottonseed oil and anhydrous acids in the constant temperature both for four hours, and then estimating the amount of acid in the oil layer and the amount of oil in the acid layer by the titration method as just described. The absolute solubility of formic acid in the organic solvents used and the solubility of the solvents in the formic acid was carried out in a similar manner.

RESULTS.

The results are given in the table below.

There are no omissions in the results obtained except preliminary experiments with acetic acid which was used for trying out methods.

In column 1 is given the concentrations expressed in grams of acid per litre of water. Columns 2 and 3

give the weight of water and oil used. In column 5 is given weight of acid in water layer, calculated from the analysis of the weighed portion of the water layer, while in Column 6 is the amount of acid for the total oil layer found in the same way. Each result in columns 5 and 6, is the average of determinations from two samples of the water or oil layer. The acid determinations in two samples of the same water layer checked within 0.5%, while in the oil layer the average deviation of the two determinations of the same layer was about 1% . The sums of the amounts of acid given in columns 5 and 6 are given in column 7. These sums should equal the amounts put in, which are given in column 4. In the dilute solutions the average error is about 1 %. The difficulty with the oil layer partly explains this deviation, while the greater error found in the more concentrated determinations may be attributed to the fact that one solvent dissolves in the other when large amounts of acid are present.

Columns 8 and 9 contain the amount of acid calculated for 100 cc. of water and oil, and the ratio of these is given in Column 10, as the partition ratio between oil and water.

The tables for the other solvents are similarly arranged.

Partition of Formic Acid between Cottonseed Oil and Water.

g.acid to 1K H_2O	Wt. H_2O	Wt. oil	Wt. HCOOH	Wt. HCOOH in H_2O	Wt. HCOOH in oil	Wt. HCOOH found	Wt. HCOOH in 1000cc H_2O	Wt. HCOOH in 1000cc oil	Direct ratio.
12-	15.417	66.854	0.1830	0.1688	0.0115	0.1803	1.094	0.0158	69.25
25+	16.938	70.530	0.4230	0.3993	0.0253	0.4248	2.3580	0.03303	71.39
41-	14.570	75.339	0.595	0.556	0.043	0.595	3.814	0.0524	72.78
46-	22.542	72.627	1.0363	0,9904	0.0471	1.0375	4.399	0.0598	72.74
61+	22.661	67.688	1.3853	1.326	0.0592	1.3852	5.849	0.0807	72.80
96+	12.055	81.518	1.1633	1.064	0.1064	1.1704	8.829	0.1209	73.08
151+	27.000	63.188	4.0771	3.945	0.1224	4.0674	14.61	0.1786	81.94
172-	6.845	5.910	1.1657	1.152	0.0130	1.1630	16.83	0.2028	85.01
271+	13.115	20.467	3.5557	3.470	0.0680	3.5380	26.44	0.3060	86.30
489-	12.617	22.868	6.1685	6.045	0.1192	6.1642	45.18	0.4806	94.00
448-	5.579	6.576	2.500	2.429	0.0323	2.4613	43.54	0.4530	(96.11)
1063+	4.543	5.051	4.827	4.747	0.0563	4.8033	104.5	1.037	100.77
1716-	3.652	5.857	6.258	6.087	0.0997	6.1867	166.6	1.568	106.24
2538-	3.1691	4.981	8.0429	7.854	0.1241	7.9781	248.15	2.297	108.03
4465	1.786	6.102	7.720	7.463	0.2222	7.6852	417.9	3.356	124.50
6623	0.7991	7.728	5.4929	5.023	0.3705	5.3935	628.6	4.420	142.22
8091	0.7295	8.599	5.8045	4.972	0.4317	5.4037	682.6	4.635	147.59

Solubility of Formic Acid in Cottonseed Oil at 25°.

Wt. Oil sample	Wt. HCOOH found	Wt. HCOOH in 100 cc. oil	Wt. HCOOH 100 g. oil
0.3154	0.02511	7.975	8.650
0.1656	0.04161	8.037	8.718
0.4437	0.03604	8.151	8.841
0.5019	0.03931	7.835	8.498
	Mean,	7.999	8.677

Solubility of Cottonseed Oil in Formic Acid. at 25° .

Wt. Acid sample	Wt. oil. found	Wt. oil in 100 cc. HCOOH	Wt. oil in 100 g. HCOOH
0.1656	0.0013	0.7912	0.7849
0.1141	0.0009	0.7951	0.7887
0.1086	0.0008	0.7450	0.7390
0.1142	0.0009	0.7936	0.7872
		Mean, 0.7812	0.7749

Partition of Acetic Acid between Cottonseed Oil and Water.

%acid in H_2O	Wt. H_2O	Wt. oil	Wt. CH_3COOH taken	Wt. CH_3COOH in H_2O	Wt. CH_3COOH in oil	Wt. CH_3COOH found	Wt. CH_3COOH in H_2O	Wt. CH_3COOH in oil	Ratio direct
21	25.841	68.321	0.5436	0.5105	0.0363	.5468	1.976	0.0489	(40.40
23+	24.319	66.229	0.5504	0.5130	0.0364	.5494	2.109	0.0507	41.59
27+	26.704	65.856	0.6962	0.6504	0.0463	.6967	2.436	0.0648	37.59
90-	27.512	71.331	2.4080	2.236	0.1711	2.4091	8.136	0.2211	36.80
96-	26.813	64.309	2.5130	2.346	0.1718	2.5168	8.917	0.2445	36.45
157-	26.681	68.802	4.1848	3.977	0.3006	4.1776	14.520	0.4029	36.03
179+	28.277	69.969	4.9751	4.636	0.3471	4.9831	16.39	0.4572	35.85
210-	24.750	67.266	5.1955	4.791	0.3940	5.1850	19.36	0.5400	35.89
431+	13.135	25.644	5.6730	5.345	0.3177	5.6627	40.67	1.143	35.67
497+	11.132	25.347	5.5344	5.178	0.3453	5.5233	46.53	1.295	36.21
912-	4.883	5.950	4.044	3.975	0.1424	4.032	98.41	2.444	40.07
1089	4.360	6.064	4.729	4.516	0.1720	4.703	103.6	(2.615)	(39.61
1861	1.387	7.574	2.5963	2.270	0.3118	2.5818	163.6	3.798	43.07
2794	1.0008	7.572	2.7940	2.361	0.4311	2.7981	235.5	5.251	44.90
4841	1.9577	5.975	9.574	8.827	0.6483	9.4753	450.9	9.959	47.25

Solubility of Acetic Acid in Cottonseed Oil at 25° .

Wt. oil sample	Wt. CH_3COOH found	Wt. CH_3COOH in 100g. oil	Wt. CH_3COOH in 100 cc. oil
0.1421	0.0808	55.59	51.25
0.0858	0.0309	56.30	51.90
0.0831	0.0299	56.29	51.89
0.0684	0.0245	55.86	51.50
0.1008	0.0345	54.34	50.10
	Mean,	55.67	51.32

Solubility of Cottonseed Oil in Acetic Acid at 25° .

Wt. sample	Wt. oil found	Wt. oil in 100g. CH_3COOH	Wt. oil in 100 cc. CH_3COOH
0.1016	0.0058	5.80	6.5
0.0996	0.0055	5.5	6.0
0.0616	0.0036	5.7	6.3
0.1373	0.0073	5.6	5.8
0.0894	0.0050	5.6	6.3
	Mean,	5.6	6.2

Partition of Propionic Acid between Cottonseed Oil and Water.

C. acid 1K H_2O	Wt. H_2O	Wt. oil	Wt. C_2H_5COOH taken	Wt. C_2H_5COOH in H_2O	Wt. C_2H_5COOH in oil	Wt. C_2H_5COOH found	Wt. C_2H_5COOH in 100cc H_2O	Wt. C_2H_5COOH in 100cc oil	Parti dir
43-	38.151	48.331	1.6199	1.347	0.2819	1.6289	3.533	0.5377	6.57
99-	39.751	42.392	3.8365	3.165	0.6580	3.8230	7.962	1.552	5.10
200+	20.051	20.095	4.0450	3.335	0.7240	4.0590	16.64	3.321	5.01
379-	15.094	20.880	5.8550	4.502	1.3580	5.8600	29.94	5.992	4.98
774-	3.416	7.705	2.7439	1.938	0.7779	2.7159	56.73	9.307	6.09
1710+	2.988	5.516	5.3112	4.438	0.8959	5.3339	148.5	14.97	9.92
3228+	0.8750	7.750	2.853	1.458	1.366	2.824	166.6	16.25	10.25
6042+	0.4755	8.9190	2.8730	0.9786	1.874	2.8526	205.8	19.37	10.62

Partition of Butyric Acid between Cottonseed Oil and Water.

% acid in H_2O	Wt. H_2O	Wt. oil	Wt. C_3H_7COOH taken	Wt. C_3H_7COOH in H_2O	Wt. C_3H_7COOH in oil	Wt. C_3H_7COOH found	Wt. C_3H_7COOH in 100 cc. H_2O	Wt. C_3H_7COOH in oil	Ratio Direc
41	16.135	24.590	0.7469	0.4526	0.2764	0.7290	2.804	1.036	2.70
98	16.568	25.095	1.6122	0.8798	0.7350	1.6148	5.310	2.700	1.96
170	6.530	6.562	1.1640	0.6615	0.4906	1.1520	10.13	6.893	1.47
417	3.139	6.755	1.3080	0.5106	0.7880	1.2990	16.27	10.75	1.51
808	3.911	6.597	3.458	1.714	1.692	3.406	35.98	23.65	1.52
1783	1.802	6.590	3.203	1.268	1.948	3.216	70.36	27.25	2.58

Partition of Isovalerie between Cottonseed Oil and Water.

g.acid 1K H_2O	Wt. H_2O	Wt. oil	Wt. C_4H_9COOH taken	Wt. C_4H_9COOH in H_2O	Wt. C_4H_9COOH in oil.	Wt. C_4H_9COOH found	Wt. C_4H_9COOH in 100cc H_2O	Wt. C_4H_9COOH in 100cc oil	Ratio Direct
66	7.762	4.149	0.5180	0.1646	0.3471	0.5117	2.121	7.714	0.2749
95	6.930	5.029	0.6600	0.1660	0.4841	0.6501	2.396	8.874	0.2700
207	6.235	5.636	1.2968	0.2080	1.091	1.2990	3.337	17.84	0.1870
479	5.247	6.177	2.5106	0.2263	2.288	2.5143	4.312	34.15	0.1262
1267	2.615	7.407	3.3142	0.1270	3.179	3.3060	4.855	39.38	0.1233
2755	2.659	3.755	7.3230	0.1603	7.200	7.3603	6.030	176.8	0.0342
2204	2.646	3.954	5.9167	0.1531	5.683	5.8414	5.788	132.5	0.0437
1562	3.826	4.174	6.0080	0.2318	5.753	5.9848	6.060	127.1	0.0477
1218	4.7324	4.0581	5.7653	0.3640	5.453	5.8170	7.694	123.9	0.0621

Solubility of Isovalerie Acid in Cottonseed Oil at 25°.

Wt. oil sample	Wt. C_4H_9COOH found	Wt. C_4H_9COOH in 100g oil	Wt. C_4H_9COOH in 100cc oil
0.6686	0.0370	5.47	5.85
1.7730	0.0974	5.43	5.81
1.4400	0.0794	5.46	5.83
	Mean,	5.45	5.83

Solubility of Cottonseed Oil in Isovalerie Acid at 25°.

Wt. sample	Wt. oil found	Wt. oil in 100 cc. C_4H_9COOH	Wt. oil in 100 g. C_4H_9COOH
0.1193	0.0147	13.01	14.05
0.1683	0 .0207	13.00	14.03
	Mean,	13.00	14.04

Partition of Formic Acid between carbon tetrachloride and Water.

g. acid 1K H_2O	Wt. H_2O	Wt. CCl_4	Wt. HCOOH taken	Wt. HCOOH in H_2O	Wt. HCOOH CCl_4	Wt. HCOOH found	Wt HCOOH in 100 cc H_2O	Wt. HCOOH in 100 cc CCl_4	Ratio	
63.5	10.291	120.32	0.6534	0.6354	0.00456	0.6399	6.175	0.00507	1218	1485
95.9	9.978	107.378	0.9572	0.9425	0.00861	0.9511	9.447	0.00861	1097	1515
215.5	9.908	135.62	2.135	2.102	0.01541	2.1174	21.21	0.0176	1094	1853
372.9	10.175	124.970	3.792	3.747	0.03416	3.7831	36.87	0.0438	838.1	1464
147.6	3.299	61.085	4.873	4.735	0.1040	4.7380	143.5	0.2654	540.8	1295
749.0	6.160	67.756	4.617	4.506	0.04213	4.5481	73.15	0.0970	754.0	1497

Solubility of formic acid in carbon tetrachloride at 25° .

Wt. of CCl_4 sample	Wt. of HCOOH found	Wt. of HCOOH 100 cc CCl_4	Wt. of HCOOH in 100 g CCl_4
0.1910	0.0069	(5.37)	(3.76)
0.3431	0.0115	5.88	3.45
0.3633	0.0119	5.31	3.40
0.3158	0.0105	5.37	3.44
	Mean,	5.55	3.42

Solubility of carbon tetrachloride in formic acid at 25° .

Wt. of HCOOH sample	Wt. of CCl_4 found	Wt. CCl_4 in 100 cc. of HCOOH	Wt. CCl_4 in 100 g of HCOOH
0.0484	0.0030	8.04	6.60
0.0934	0.0062	8.35	6.95
0.0918	0.0063	8.96	7.31
	Mean,	8.55	6.95

Partition of Formic Acid between Toluene and Water

g. acid 1K H_2O	Wt. H_2O	Wt. C_7H_8	Wt. HCOOH taken	Wt. of HCOOH in H_2O	Wt. HCOOH in C_7H_8	Wt. HCOOH found	Wt. HCOOH in 100cc. H_2O	Wt. of HCOOH in 100cc. C_7H_8	Ratio	
55.6	21.04	79.94	1.174	1.177	0.0118	1.188	5.594	0.01279	437.2	453.7
94.1	20.43	64.20	1.799	1.761	0.0158	1.779	8.618	0.0212	406.3	485.0
202.3	10.319	88.00	2.086	2.039	0.0498	2.084	19.76	0.0487	405.1	517.4
402.2	9.210	84.70	4.257	4.148	0.1166	4.264	45.03	0.1185	380.0	538.1
744.2	5.618	30.87	4.181	4.019	0.0837	4.1027	73.13	0.2335	313.2	502.4
150.3	3.276	32.68	5.186	4.934	0.2391	5.0731	147.60	0.6298	234.3	426.3

Solubility of formic acid in Toluene at 25°.

Wt. C_7H_8 Sample	Wt. HCOOH found	Wt. HCOOH in 100cc. C_7H_8	Wt. HCOOH in 100g C_7H_8
0.2815	0.0284	9.64	11.20
0.3795	0.0376	9.45	10.98
0.2986	0.0295	9.43	10.96
0.3565	0.0358	0.61	11.17
	Mean,	9.53	11.15

Solubility of Toluene in formic acid at 25°.

Wt. HCOOH sample	Wt. C_7H_8 found	Wt. C_7H_8 in 100cc. HCOOH	Wt. C_7H_8 in 100 g. HCOOH
0.1793	0.0149	11.05	9.08
0.1323	0.0110	11.03	9.06
0.0851	0.0071	11.08	9.10
	Mean	11.05	9.08

Partition of Formic Acid between Benzene and Water.

g. acid in K H_2O	Wt. H_2O	Wt. C_6H_6	Wt. HCOOH taken	Wt. HCOOH in H_2O	Wt. HCOOH in C_6H_6	Wt. HCOOH found	Wt. HCOOH in 100cc H_2O	Wt. HCOOH in 100cc C_6H_6	Ratio	
55.2	20.613	74.212	1.138	1.448	0.0126	1.159	5.569	0.0139	400.0	420.5
64.7	11.460	89.069	0.7420	0.7165	0.01748	0.7350	6.252	0.01713	364.9	395.7
110.0	19.961	82.543	2.195	2.1920	0.0329	2.224	10.97	0.03478	315.4	380.2
158.5	21.715	65.425	3.444	3.432	0.0382	3.470	15.80	0.0507	311.6	397.6
229.1	23.386	51.661	6.506	6.437	0.04339	6.481	22.67	0.07245	313.0	420.1
426.7	10.301	28.708	4.395	4.258	0.04489	4.302	41.34	0.1364	303.1	438.2
718.1	12.707	32.925	9.126	8.894	0.1060	9.000	70.97	0.2808	249.2	416.7
155.8	3.872	40.730	5.096	4.695	0.3279	5.023	143.5	0.7024	204.3	396.7

Solubility of Formic Acid in Benzene at 25°.				Solubility of Benzene in Formic Acid at 25°.			
Wt. C_6H_6 sample	Wt. of HCOOH found	Wt. of HCOOH in 100 g C_6H_6	Wt. of HCOOH in 100 g C_6H_6	Wt. of C_6H_6 taken	Wt. of C_6H_6 found	Wt. of C_6H_6 in 120 cc. HCOOH	Wt. of C_6H_6 in 120 g. HCOOH
0.3718	0.0341	12.49	14.32	0.1825	0.0238	18.21	15.00
0.3300	0.0416	12.57	14.41	0.0992	0.01312	18.50	15.34
0.3950	0.0502	12.69	14.54	0.1455	0.0169	18.13	14.93
0.4277	0.0537	12.51	14.34	0.0930	0.0122	18.67	15.38
0.4197	0.527	12.54	14.38		Mean,	18.37	15.13
	Mean,	12.56	14.39				

Partition of Formic Acid between Water and Bromoform at 25°.

g. acid 1 K H_2O	Wt. H_2O	Wt. HCOOH taken	Wt. HCOOH in H_2O	Wt. HCOOH in $CHBr_3$	Wt. HCOOH found	Wt. HCOOH in 100 cc. H_2O	Wt. HCOOH in 100 cc. $CHBr_3$	Ratio	
56.1	9.746	243.02	0.5734	0.2771	0.5855	3.165	0.3289	9.62	5.98
107.2	10.280	189.078	1.123	0.3407	1.102	7.405	0.5197	14.25	7.37
150.5	11.029	177.069	1.660	0.3131	1.648	12.14	0.5129	23.30	12.30
373.5	10.386	192.304	3.898	0.7580	3.881	30.06	1.137	26.44	10.00
709.4	5.286	53.508	3.792	0.3630	3.741	63.91	1.957	32.67	9.93
135.3	3.430	58.994	4.762	0.7142	4.674	115.4	3.491	33.06	7.98

Solubility of Formic Acid in Bromoform at 25°.

Wt. of $CH Br_3$ sample	Wt. HCOOH found	Wt. of HCOOH in 100 cc. $CH Br_3$	Wt. of HCOOH in 100 g. $CH Br_3$
1.9684	0.0475	7.13	2.47
1.2830	0.0310	7.13	2.47
3.2351	0.0767	7.00	2.42
	Mean	7.07	2.45

Solubility of Bromoform in Formic Acid at 25°.

Wt. of HCOOH taken	Wt. of $CH Br_3$ found	Wt. of $CH Br_3$ in 100 cc. HCOOH	Wt. of $CH Br_3$ in 100 g. HCOOH
0.1301	0.0362	30.68	25.21
0.1085	0.0220	30.96	25.44
	Mean	30.82	25.32

Partition of Formic Acid between Carbon Disulphide and Water

g. acid in H_2O	Wt. H_2O	Wt. CS_2	Wt. HCOOH taken	Wt. HCOOH in H_2O	Wt. HCOOH in CS_2	Wt. HCOOH found	Wt. HCOOH in 100 c.c. H_2O	Wt. HCOOH in 100 c.c. CS_2	Ratio
50.2	10.239	122.65	0.5145	0.5117	0.003900	0.5157	4.997	0.00400	1250
93.5	10.485	115.34	0.9806	0.9652	0.006613	0.9718	9.209	0.007228	1274
172.7	11.361	122.04	1.9620	1.942	0.01281	1.9558	17.09	0.01323	1289
353.0	10.214	111.978	3.583	3.536	0.02403	3.560	34.63	0.02706	1280
733.5	5.406	125.27	3.966	3.850	0.05497	3.915	71.24	0.05527	1289
126.0	6.244	121.75	7.763	7.565	0.09122	7.7656	121.1	0.09439	1284

Solubility of Formic Acid in Carbon Disulphide at 25°.				Solubility of Carbon Disulphide in Formic Acid at 25°.			
Wt. of Sample	Wt. HCOOH found	Wt. HCOOH in 100cc. CS_2	Wt. HCOOH in 100g. CS_2	Wt. sample	Wt. CS_2 found	Wt. of CS_2 in 100 gs. HCOOH	Wt. of CS_2 in 100 g. HCOOH
2.4628	0.0313	1.62	1.29	0.0631	0.0604	5.43	4.47
1.9878	0.0240	1.58	1.28	0.1429	0.1398	5.69	4.95
2.6070	0.0311	(1.52)	(1.21)		Mean,	5.56	4.83
4.7033	0.0549	(1.49)	(1.18)				
4.9431	0.0569	(1.46)	(1.16)				
7.461	0.0959	1.62	1.29				
	Mean,	1.61	1.28				

Solubility of Formic Acid in Xylene at 25° .				Solubility of Xylene in Formic Acid at 25° .			
Wt. of C_8H_{10} sample	Wt. of HCOOH found	Wt. HCOOH in 100cc C_8H_{10}	Wt. HCOOH in 100 g. C_8H_{10}	Wt. HCOOH sample	Wt. C_8H_{10} found	Wt. C_8H_{10} in 100cc. HCOOH	Wt. C_8H_{10} in 100g. HCOOH
0.5440	0.0442	7.6	8.83	0.1009	0.0083	8.10	6.81
0.3535	0.3251	7.5	8.7	0.0790	0.0057	9.46	7.77
0.4480	0.0357	7.5	9.7		Mean,	8.78	7.29
	Mean,	7.5	8.7				

Partition of Formic Acid between Xylene and Water.

g. acid in H_2O	Wt. H_2O	Wt. C_8H_{10}	Wt. HCOOH taken	Wt. HCOOH in H_2O	Wt. of HCOOH in C_8H_{10}	Wt. HCOOH found	Wt. HCOOH cc. W_2O	Wt. HCOOH C_8H_{10}	Ratio	
53.8	10.419	83.55	0.5608	0.5521	0.0190	0.5711	5.300	0.01970	268.7	278.5
56.8	9.867	94.58	0.5930	0.5855	0.0225	0.5580	5.428	0.02053	263.2*	272.8
101.7	11.245	88.25	1.185	1.158	0.03619	1.194	10.30	0.03638	270.3*	301.9
107.7	9.891	76.12	1.066	1.048	0.03190	1.079	10.60	0.0363	291.7	311.5
183.8	10.411	71.74	1.889	1.835	0.04113	1.876	17.63	0.04973	354.5*	384.2
187.1	10.849	79.05	2.036	2.006	0.04390	2.049	18.49	0.05367	344.5	374.7
346.6	10.029	67.24	3.576	3.460	0.07784	3.537	34.50	0.1002	344.3	386.3
368.9	10.336	69.27	3.795	3.697	0.07764	3.7746	35.93	0.09716	(369.7)*	(414.3)
702.1	6.136	30.50	4.308	4.171	0.06803	4.239	67.97	0.1934	350.0	407.5
705.2	5.861	38.13	4.248	4.125	0.0963	4.251	70.13	0.2190	345.9	375.7
130.1	3.870	29.86	5.036	4.760	0.1498	4.909	12.38	0.4349	282.8	343.7
134.8	3.994	38.84	5.382	5.026	0.1923	5.218	125.8	0.4293	(293).2	363.6
181.6	3.360	84.32	4.830	4.036	0.5611	4.613	151.70	0.5769	263.0	322.1

*

Partition of Acetic Acid between Kerosine and Water.

g. acid in H_2O	Wt. H_2O	Wt. kerosene	Wt. HCOOH taken	Wt. HCOOH in H_2O	Wt. HCOOH kerosene	Wt. HCOOH found	Wt. HCOOH in 100cc. H_2O	Wt. HCOOH in 100cc Ker.	
102.7	7.110	32.024	7.300	0.7127	0.02164	0.7343	11.02	0.05400	185.6
211.6	6.027	30.676	1.392	1.236	0.05796	1.3930	20.51	0.1508	136.0
392.7	6.786	29.831	2.665	2.532	0.1332	2.6652	37.31	0.3566	104.6
930.7	2.503	8.479	2.330	2.214	0.09804	2.3120	88.43	0.9234	95.8
155.1	2.819	6.243	4.273	4.089	0.1217	4.211	145.0	1.557	93.2

Solubility of Acetic Acid in Kerosene at 25°.

Wt. Sample	Wt. CH_3COOH found	Wt. CH_3COOH in 100cc. Ker.	Wt. CH_3COOH in 100g. Ker.
1.0690	0.1909	17.36	21.74
0.7638	0.1367	17.41	21.80
	Mean,	17.38	21.77

Solubility of Kerosene in Acetic Acid at 25°.

Wt. sample	Wt. kerosine found	Wt. kerosine in 100cc. CH_3COOH	Wt. Ker. in 100g. CH_3COOH
0.0735	0.0082	15.28	12.56
0.0802	0.0088	15.01	12.30
	Mean,	15.14	12.43

Partition of formic Acid between Kerosene and Water.

g.acid 1 K H_2O	Wt. H_2O	Wt. kerosene	Wt. HCOOH taken	Wt. HCOOH in H_2O	Wt. HCOOH in ker.	Wt. HCOOH found	Wt. HCOOH in 1000 H_2O	Wt. HCOOH in kerosene	
223.3	10.634	65.717	2.324	2.316	0.00648	2.322	21.80	0.00788	2766
493.5	9.801	72.723	4.452	4.388	0.01586	4.404	44.76	0.01719	2605
704.7	9.778	65.189	6.283	6.224	0.02146	6.245	63.65	0.02628	2422
814.9	2.547	7.422	1.945	1.936	0.00308	1.939	76.00	0.03810	2001
152.9	2.725	5.645	4.160	4.060	0.00714	4.067	149.0	0.1008	1477
203.0	3.153	30.950	6.400	6.200	0.05358	6.254	196.6	0.1382	1422

Solubility of formic acid in kerosene at 25°.

Wt. sample	Wt. HCOOH found	Wt. HCOOH in 1000 ker.	Wt. HCOOH in 100 g. ker.
3.3003	0.0294	0.7181	0.8994
2.9977	0.0267	0.7231	0.9055
	Mean,	0.7206	0.8974

Solubility of kerosene in formic acid at 25°.

Wt. sample	Wt. kerosene found	Wt. kerosene in 1000 HCOOH	Wt. Kerosene in 100 g. HCOOH
0.1003	0.0015	1.85	1.52
0.0681	0.0011	1.95	1.60
	Mean,	1.90	1.56

DISCUSSION OF RESULTS.

The partition coefficient law and the Boedecker modification $\frac{C^{x}_{water}}{C_{solvent}} = K$ has been discussed by Von Gerogrevius.[1] He finds for partition of formic acid between benzene and water that $x = 1$, that is the acid is equally associated in both solvents. By freezing point experiments he showed that formic acid is monomolecular in benzene and hence unassociated in water. In calculating the figures in the last column of the above tables of benzene, toluene, xylene, carbontetrachloride, and bromoform, the equivalent formula $\frac{C_{water}}{C^{y}_{solvent}} = K$, has been used and the value of y, which gives the most nearly constant value of K has been found by trial. For partition of formic acid between water and benzene, toluene, and carbontetrachloride, the best values of y appear to be 0.85 . The xylene gave a value of 0.95 for y, while the bromoform gave the still higher value of 1.4 .

The last value may partially explain the exception which will be referred to later in connection with the bromoform curve.

The results are brought together in plotted form on the following pages.

On page 33 are plotted the results obtained from partitioning the lower fatty acids between cottonseed oil and water. The numbe of carbon atoms are indicated by the abscissas, while the ordi-

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1. Zeit. Physik. Chem. 84, 353, (1913).

notes give the square roots of the partition ratios. The partition ratios used for the different acids are taken at approximately the same concentrations -- 300 g. acid per kilogram of water.

The next plot gives the results of the same partition work with the fatty acids, but here the partition ratios of each acid is plotted against the corresponding concentrations, expressed in grams of acid per 100 g. of total water used.

In the third plot are found the results which are obtained from partitioning formic acid between water and the solvents: benzene, toluene, xylene, carbontetrachloride, carbonbisulphide, bromoform, cottonseed oil, and kerosene oil. The products of the solubility of formic acid in the different solvents and their respective ratios have been plotted against the concentrations expressed in grams of acid per 100 g. of total water used.

The last plot is similar to the third where acetic acid is used instead of formic acid.

Experiments showed that propionic, butyric, and isovaleric acids mixed with the oils and also with the organic solvents in all proportions. This prevented the determinations of their direct solubilities, and hence it was not possible to use them in solving the problem in question. Wroth and Reid, partitioned the lower alcohols between cottonseed oil and water, and found that the ratio decreased as the number of carbon atoms increased. In view of this fact it was interesting to see if a similar relation was true with the corresponding acids when partitioned be-

tween the same two solvents. The plot found on page 35 shows that the same relation was found as in the case of the alcohols.

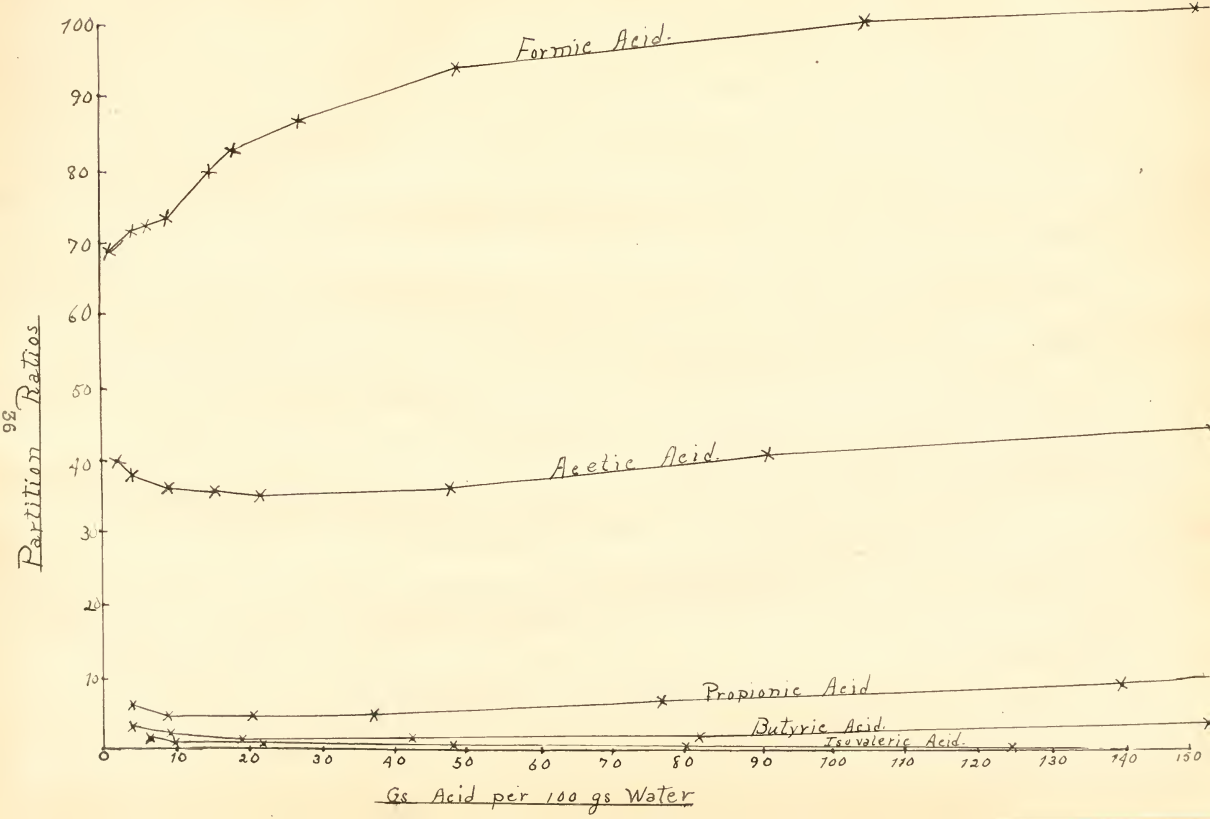
The next plot shows how the ratios vary with the concentrations. The acetic, propionic, and butyric acid curves have a minimum. The ratios of formic acid increase regularly with concentrations after a dilution of about 300 g. acid per kilogram of water is reached, while the isovaleric ratios decreases with the increased concentrations.

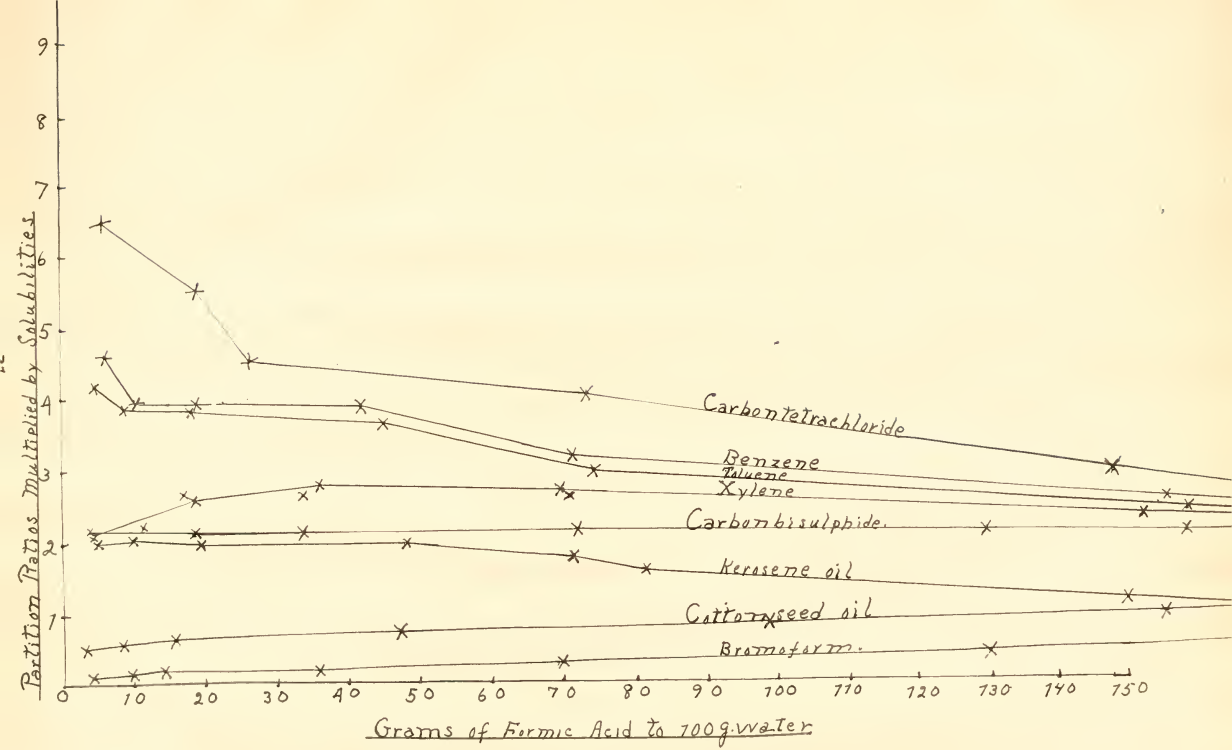
Since the purpose of this investigation was to inquire into the nature of the so-called infinite soluble substances, the partition work of formic acid with the solvents mentioned, has been plotted as shown on page 37 and as explained on page 33. The ordinates would then seem to express the solubility of formic acid in water.

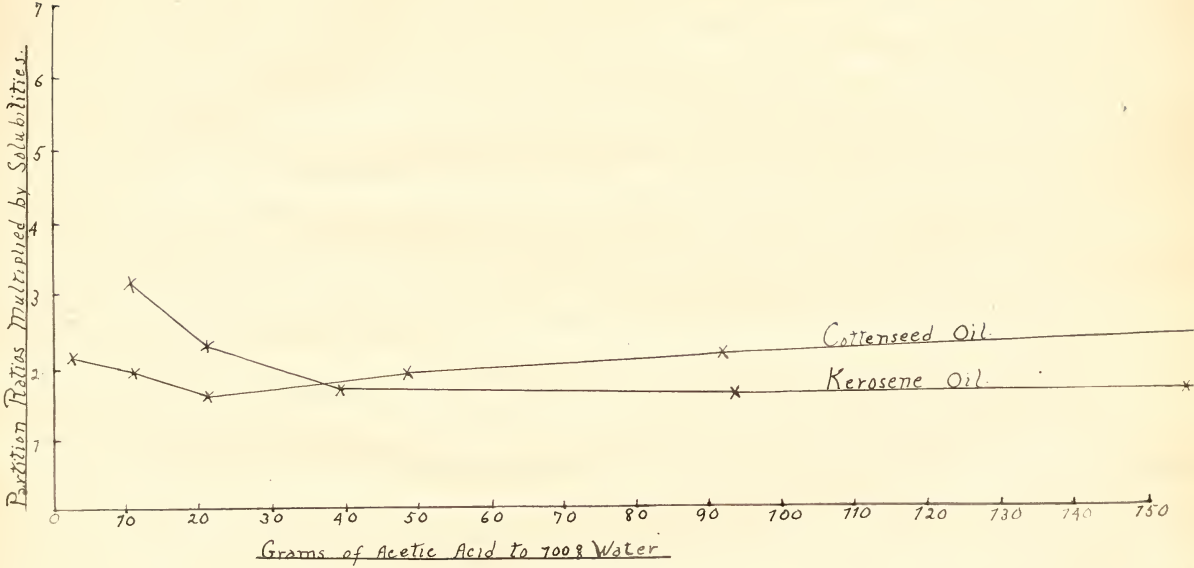
If formic acid has a definite solubility in water, it might be expected, at first thought, that all these curves should coincide; but when the many influences such as ionization, association, hydration, salt effect, etc., which are common to solutions, are taken into consideration, it is quite plain that a coincidience would be possible only under ideal conditions.

It was expected that benzene, toluene, and xylene would approach most nearly to ideal conditions since the three compounds are similar in their chemical nature. From the figures it appears that the benzene and toluene curves run nearly parallel and at a very short distance apart, and that if produced, they would intersect at about 1600.

Square roots of Partition Ratios
Number of Carbon Atoms
in Acids


Partition Ratios
Formic Acid.
Acetic Acid.
Propionic Acid
Butyric Acid.
Isovaleric Acid.
Gs Acid per 100 gs Water
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150


Partition Ratios Multiplied by Solubilities
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Grams of Formic Acid to 100 g. water
Carbon tetrachloride
Benzene
Toluene
Xylene
Carbon bisulphide.
Kerosene oil
Cotton seed oil
Bromoform.


Partition Ratios Multiplied by Solubilities.
7
6
5
4
3
2
1
Cottenseed Oil.
Kerosene Oil.
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Grams of Acetic Acid to 100g Water

It is remarkable that the xylene curve, which starts much lower and with the opposite curvature, runs to the benzene and toluene curves for the greater concentrations.

The curves for carbontetrachloride, benzene, xylene, and carbonbisulphide show a tendency to converge toward a point having an ordinate of about 1600. This would indicate a solubility of formic acid of something like 1600 g. in 100 cc. of water. This convergency toward a common value would lend much support to the idea that this is the real solubility of formic acid in water, were it not for the exceptions which appear with the other oils. The curve given by cottonseed oil starts low, but has a steady upward trend and might possibly be supposed to approach the others at some point far beyond the limits of the diagram. The bromoform curve is of the same form, but is so low that no approach to the common point is apparent. This is all the more remarkable as bromoform resembles chemically carbontetrachloride. On the other hand bromoform has a far greater solubility in formic acid than the other solvents used, and also a greater exponent in the Boedecker formula as mentioned on page 32. These two facts may partially expalin its anomalous behavior. The kerosene curve is the most puzzling. For a time it runs close to the carbonbisulphide curve, but deviates far from it for concentrated solutions and seems to take a direction entirely away from any of the others. Since kerosene is a mixture of hydrocarbons of various

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1. See table of solubilities below.

kinds, its exceptional behavior is not so surprising.

The next set of curves represent the results obtained from partitioning acetic acid between water and cottonseed oil and kerosene oil. In the plotting, the ordinates and abscissas have the same significance as in the preceding case. These curves appear to intersect at a point whose ordinate is about 1800. From what has been said in the preceding case this would indicate that 1800 grams of acetic acid should dissolve in 100 cc. of water. These two solvents have offered exceptions in the case of formic acid and thus it is not safe to draw very definite conclusions from them, and especially since the data are so meager. Further work will have to be done. Thus far no other solvents have been found which may be used with the acetic acid.

The results obtained show that we are dealing with quite complex phenomena, which will require much work before they are cleared up. The work is being continued in this laboratory.

Summary.

1. The partition ratio of formic acid between water and the solvents, benzene, toluene, and kerosene decreased with increased concentration, while it increased with increased concentration in the case bromoform and xylene. With cottonseed oil the ratio seemed to have a minimum .

2. The partition ratios of acetic, propionic, butyric, and isovaleric acids between water and cottonseed oil have a minimum.

3. The partition ratio of acetic acid between water and kerosene oil decreases with increased concentration.

4. The partition ratios of formic, acetic, propionic, butyric, and isovaleric acids between cottonseed oil and water decrease with increasing number of carbon atoms.

5. Solubilities.

Solvent	g HCOOH/100cc. solvent	g. solvent/100cc HCOOH
Cottonseed oil	7.99	5.6
Benzene	12.56	18.37
Toluene	9.53	11.05
Xylene	7.50	8.78
Carbontetrachloride	5.35	8.55
Carbonbisulphide	1.61	5.56
Bromoform	7.07	30.82
Kerosene b.p.180-260°.	0.78	1.90

6. The solubility of acetic acid in cottonseed oil and kerosene oil is 55.77 and 17.21 g. per 100cc. of the oils at 25°.

7. The solubility of isovaleric acid in water is 5.45 g. per 100 cc. of water at 25° and that of water in isovaleric acid is 13 g. per 100 cc. isovaleric acid at 25°.

8. By using the above data an attempt has been made to calculate the ideal solubilities of the lower acids in water.

Biography.

Neil Elbridge Gordon was born at Spafford, New York, October 7, 1886. He was graduated from Homer High School in 1904, and from Syracuse University, Syracuse, New York, in 1911 with a degree of Ph.B, and in 1912 with a degree of A.M. He has spent four Summer Schools in study of Chemistry - three at Syracuse University and one at Johns Hopkins University. At Syracuse University he has been an assistant in mathematics for two years, and an instructor in mathematics during four summer sessions. In the fall of 1913 he was appointed instructor of science at The Park School, Baltimore, Md. During his three years teaching at The Park School, he took graduate lectures in chemistry at The Johns Hopkins University and did laboratory work Saturdays. The past year he has taken full graduate work at The Johns Hopkins University.